REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	06/05/03	Final, Aug. 1, 1999 - Jan. 31, 2003

4. TITLE AND SUBTITLE	5. FUNDING NUMBERS
Structural, Electronic, and Dynamic Properties of Metallic Supercooled Liquid and Glasses Studied by NMR	DAAD 19-99-1-0328
6. AUTHOR(S) Yue Wu	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of North Carolina, Chapel Hill, NC 27599-3255	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211	10. SPONSORING / MONITORING AGENCY REPORT NUMBER 39870-MS • 3

11. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12 a. DISTRIBUTION / AVAILABILITY STATEMENT	12 b. DISTRIBUTION CODE
Approved for public release; distribution unlimited.	

13. ABSTRACT (Maximum 200 words)

Metallic glasses possess unique mechanical and magnetic properties such as extremely high hardness and have novel applications in many areas including national defense. What prevents the widespread use of metallic glasses is the difficulty in achieving the glassy form due to the low glass forming ability (GFA) of most metallic alloys. The search of new BMGs requires an understanding of GFA on the atomic level and over a wide range of timescales. In this study we used nuclear magnetic resonance (NMR), along with other techniques, to study both structures and atomic motions in Zr-based and Pd-based BMG systems over the entire temperature range from the liquid state down to the glassy state. We observed a clear evidence of a dynamic crossover at temperature T_c above the glass transition temperature T_g. This observation shows that below T_c atomic rattling within cages formed by neighboring atoms freezes rapidly. It demonstrates that such dynamic crossover plays a crucial role in glass transition. Comprehensive studies using NMR, x-ray diffraction, and differential scanning calorimetry revealed the details of nucleation and growth processes in such BMGs and provided useful clue for improving GFA of metallic alloys.

14. SUBJECT TERMS	15. NUMBER OF PAGES
Metallic glasses, supercooled liquid, bulk metallic glasses, NMR spectroscopy	16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT	18. SECURITY CLASSIFICATION ON THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)
Prescribed by ANSI Std. 239-18
298-102

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

Statement of the problem studied

The focus of our study is to investigate the structure and dynamics in metallic supercooled liquids and glasses in order to understand the glass forming ability (GFA) of metallic systems. Metallic glasses possess unique properties such as mechanical and magnetic properties but the widespread use of metallic glasses is hindered by the very low GFA of most metallic alloys. Nuclear magnetic resonance (NMR) is an ideal tool for investigating both structure and dynamics. Using NMR, along with x-ray diffraction (XRD) and differential scanning calorimetry (DSC), we have investigated systematically the structure, microscopic dynamics, and nucleation and growth processes of Zr-based and Pd-based bulk metallic glasses (BMG). These studies provide important information on the GFA of metallic glasses.

Summary of the most important results

Slow atomic motion in Pd-based systems: diffusion

NMR measurement of slow atomic motions near T_g has been carried out using stimulated echo technique in PdNiCuP BMG. Similar technique has been used earlier to detect slow Be atomic motions in Vit1 and Vit4 BMG. We measured the hopping rate Ω of phosphorus atoms in various Pd-based BMG. As an example, the temperature dependence of $\Omega=1/T_{SE}$ in BMG $Pd_{43}Cu_{27}Ni_{10}P_{20}$ is shown in Figure 1 (a). The effect of diffusion near T_g=570 K is clearly visible by NMR. Systematic measurements of Ω versus $1/T$ were carried out for several Pd-based BMG systems and the results are shown in Fig. 1 (b). Again, most systems exhibit activated behavior of motion with the same activation energy of 1.34 eV except in $Pd_{41.75}Cu_{41.75}P_{16.5}$. $Pd_{40}Ni_{40}P_{20}$ exhibits the slowest P motion compared to $Pd_{43}Ni_{10}Cu_{27}P_{20}$, $Pd_{40}Ni_{10}Cu_{30}P_{20}$, and $Pd_{41.75}Cu_{41.75}P_{16.5}$. $Pd_{40}Ni_{40}P_{20}$ possesses similar P motion as that in $Pd_{47}Ni_9Cu_{25}P_{19}$. Although the activation energy is the same (except in $Pd_{41.75}Cu_{41.75}P_{16.5}$), the pre-exponential factor changes significantly from system to system.

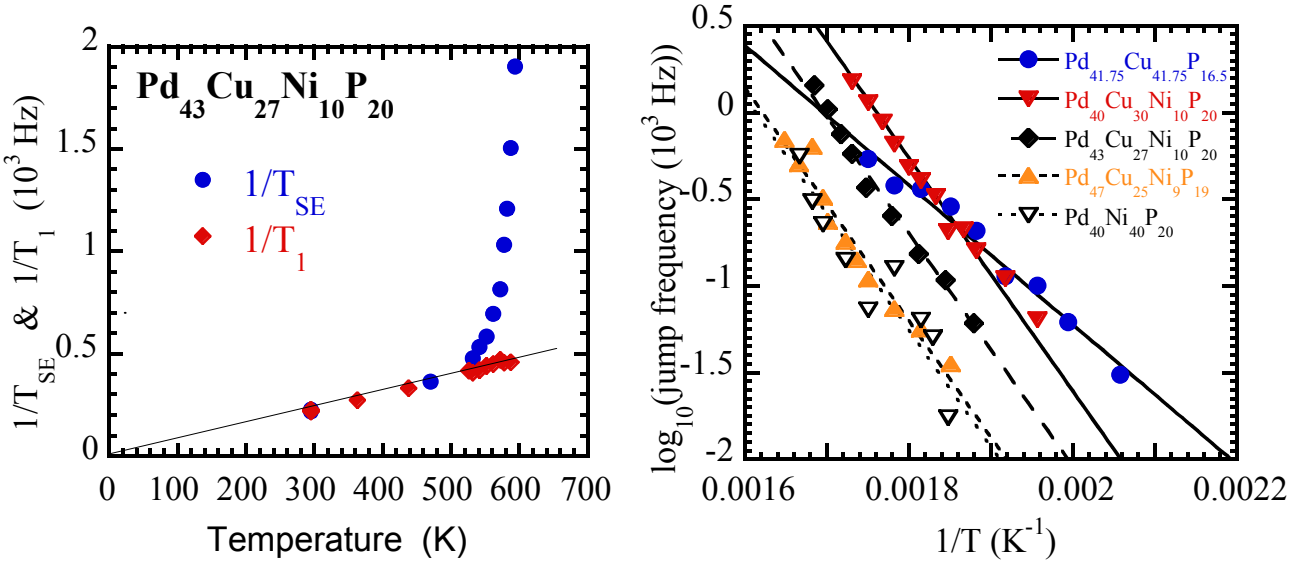

Figure 1: (a) ^{31}P stimulated echo decay rate $1/T_{SE}$ (hopping rate) versus temperature in $Pd_{43}Ni_{10}Cu_{27}P_{20}$. (b) $\Omega(T)$ of various Pd-based BMGs. The activation energy is 1.34 eV except in $Pd_{40}Cu_{40}P_{20}$.

It is important to understand what factors influence this pre-exponential factor. Based on Fig. 1 (b), a correlation can be established. P motion is linked to the Cu content, namely, the higher the Cu content the faster P hopping. Starting from $Pd_{40}Cu_{30}Ni_{10}P_{20}$, it is interesting to see that substitutions of Cu by Pd or Ni reduce P motion. Phosphorus diffusion plays an important role in the slowdown of dynamics and structural relaxation and is directly related to the GFA. The influence of such composition dependence of P diffusion provides important information on the factors influencing the GFA.

Fast atomic motion in Pd-based systems: microscopic dynamics

With regard to the microscopic dynamics of crystal melting, the Lindemann criterion states that melting occurs when the root-mean-square atomic displacement $\sqrt{<u^2>}$ caused by vibrations reaches a certain fraction of the equilibrium atomic spacing. Define $\sqrt{<u^2>}$ as a measure of the dynamically induced deviation of atomic spacing from the equilibrium value, thus excluding the effect of diffusion, $<u^2> \propto T$ is expected to be valid in both solids and dense liquids of predominantly harmonic systems. Therefore, the identification of a temperature region with rapidly changing $<u^2>$ bridging two $<u^2> \propto T$ regions could be viewed as a signature of liquid-like to solid-like transition in supercooled liquids. For experimental investigations of such transition, dense metallic supercooled liquid is an ideal system compared to other systems such as molecular systems. Metallic liquids are simple liquids of close-packed atoms without internal degree of freedom where atomic vibrations are expected to be predominantly harmonic even in the liquid state near T_{liq}. This makes the recognition of liquid-like to solid-like transition through $<u^2>$ versus T transparent. Mode-coupling theory (MCT) predicts the existence of such a transition in simple liquids. It predicts that the onset of this transition upon cooling occurs at a critical temperature T_c significantly above T_g. Such a liquid-like to solid-like transition through the observation of $<u^2>$ in metallic supercooled liquids has not been reported. We developed an NMR technique to measure the effect of $<u^2>$ in metallic $Pd_{43}Ni_{10}Cu_{27}P_{20}$ over a wide temperature range. A clear liquid-like to solid-like transition is observed with a transition region ranging from a temperature significantly above T_g down to around T_g.

Figure 2 (a) shows the room temperature (RT) ^{31}P NMR spectra of the glassy $Pd_{43}Ni_{10}Cu_{27}P_{20}$ sample as well as the spectrum in the liquid state. For comparison, the spectrum of the crystallized sample is also shown. Here, the shift of the peak originated from the Knight shift K is a direct measure of $<u^2>$ in the supercooled liquid state. Figure 2 (b) shows the observed average shift K from RT up to $T>T_{liq}$. The shift changes linearly with temperature both above 700 K, with a slope of 0.75 ppm/K, and below T_g, with a slope of 0.27 ppm/K. The much steeper change of K with temperature between 580 K and 700 K in Fig. 2 (b) is a very interesting feature. It clearly separates the two temperature regions, namely, the liquid-like region above 700 K and the solid-like region below 580 K. It demonstrates that local atomic motion present in the liquid state persists in the supercooled liquid state down to 700 K below which it decreases rapidly and reaches the level of local atomic motion present in the glassy state near T_g. It shows that the gradual freezing of certain local atomic motions starts at a temperature significantly above T_g. A candidate of such local atomic motion is the fast β-process associated with rattling motions of atoms confined in temporary cages formed by neighboring atoms. Based on mode-coupling theory (MCT), this motion is predicted to induce a temperature dependent $\sqrt{<u^2>}$ below T_c given by

$$\sqrt{<u^2>} = u_c\left(1-\frac{1}{2}a\sqrt{(T_c-T)/T_c}\right) \qquad (1)$$

where a>0 and u_c is the magnitude of motion at and above the critical temperature T_c. A fit of K is shown in Fig. 2 (a) using Eq. (1). Our results are consistent with MCT. Further studies of BMG with different compositions will be reveal the nature of such critical slowdown in microscopic dynamics.

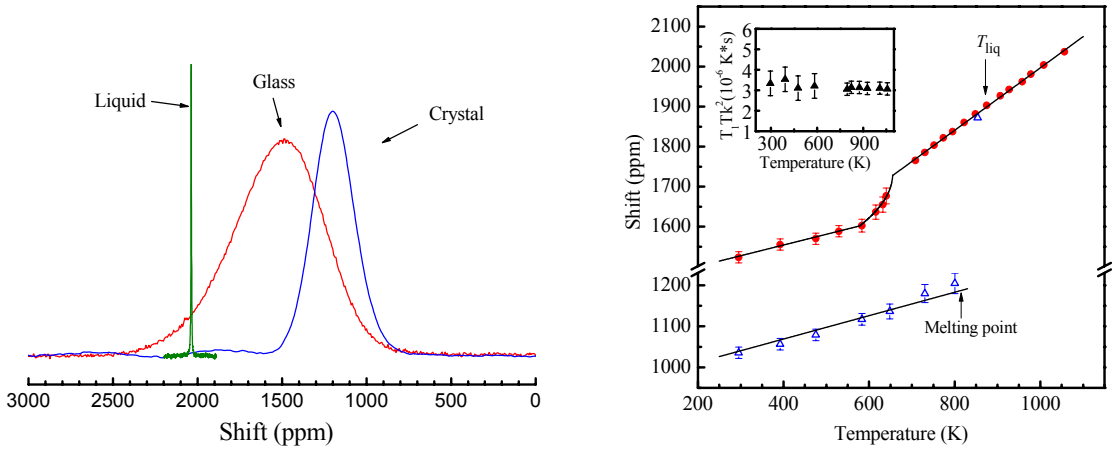

Figure 2. (a) ^{31}P NMR spectra of the glassy and crystallized samples at RT, detected using the Hahn echo sequence (*14*) (90˚-10μs-180˚-10μs-detection), and the spectrum of the liquid state taken at 1057 K. The shift K is defined as $K \equiv (\nu - \nu_{\text{ref}})/\nu_{\text{ref}}$ where ν is the frequency and ν_{ref} is the resonance frequency of the reference sample (85% H_3PO_4 for ^{31}P). The RT spectrum has a full-width-at-half-height linewidth of about 630 ppm (100 kHz at 9.4 Tesla and 50 kHz at 4.7 Tesla). (b) The average shift K in the liquid, supercooled liquid, and glassy states (solid circle) as well as that of the crystallized sample (open triangle). The solid line is a fit using Eq. (1) with $T_c = 655\,\text{K}$. The inset shows T_1TK^2 versus T. T_1 was measured using the saturation recovery method.

Crystallization in $Pd_{43}Ni_{10}Cu_{27}P_{20}$ Melts

$Pd_{43}Ni_{10}Cu_{27}P_{20}$ alloy has the lowest critical cooling rate of all BMGs discovered thus far. The high stability of these quaternary PdNiCuP alloys against crystallization leads to a large experimentally accessible time and temperature window for investigations of the transformation behavior under isothermal conditions from the supercooled liquid into crystalline phases. Statistical methods are powerful tools to investigate crystallization of supercooled liquids. One approach is to divide the sample into small particles. It was found that much deeper undercooling can be achieved in samples consisting of a large number of small isolated droplets than in one large sample. We studied, among others, the crystallization of a collection of a few hundred $Pd_{43}Ni_{10}Cu_{27}P_{20}$ particles that are 100 to 350 μm in diameter and are separated from each other by Al_2O_3 particles (50 μm in diameter) and B_2O_3.

Figure 3 (a) shows the heat release detected by DSC as a function of the length of time the $Pd_{43}Ni_{10}Cu_{27}P_{20}$ particles were held isothermally at 733 K. Interestingly, crystallization of the particles does not occur simultaneously but spreads out over more than 1.5×10^5 s. From this measurement the number of crystallization events occurring within time interval of 6000 s is plotted as a function of time as shown in Fig. 3 (b). The number of crystallization events is Poisson distributed. Since individual crystallization events are observed, the crystallization of each particle must be triggered by a single nucleation event. Otherwise, averaging over many nucleation events will smear out the wide spread in time of crystallization events. From these data the nucleation rate I_{SS} as a function of temperature can be directly measured.

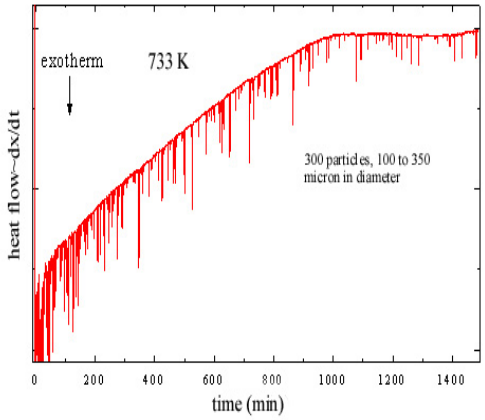

Figure 3 (a)

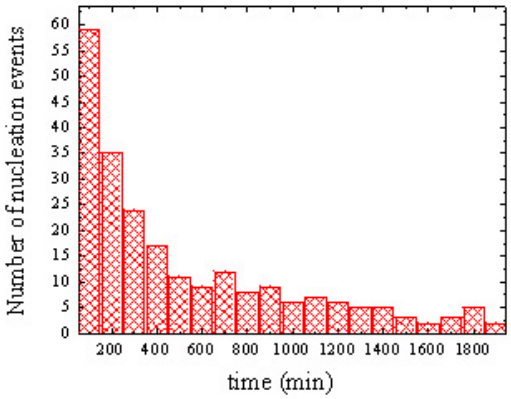

Figure 3 (b)

With the 300-particle sample isothermal crystallization studies were performed at temperatures covering the entire supercooled liquid temperature range as shown in Fig. 4. The crystallization of the individual particles at 753 K is spread out over 78000 s and 65% of the particles do not crystallize within this time period. At 723 K the data look very similar (different vertical scale). However, the time over which the events are spread out decreases to 42000 s and only 10% did not crystallize over this time period. Lowering the temperature by only 5 degrees to 718 K results in a very different DSC signal as shown in Fig. 4. More than 95% of the sample crystallized simultaneously after 240 s within 200 s. The residual liquid particles do crystallize within 3×10^3 s. For lower temperatures the crystallization event of the 300 particle sample can not be distinguished from a sample that contains just one bulk particle.

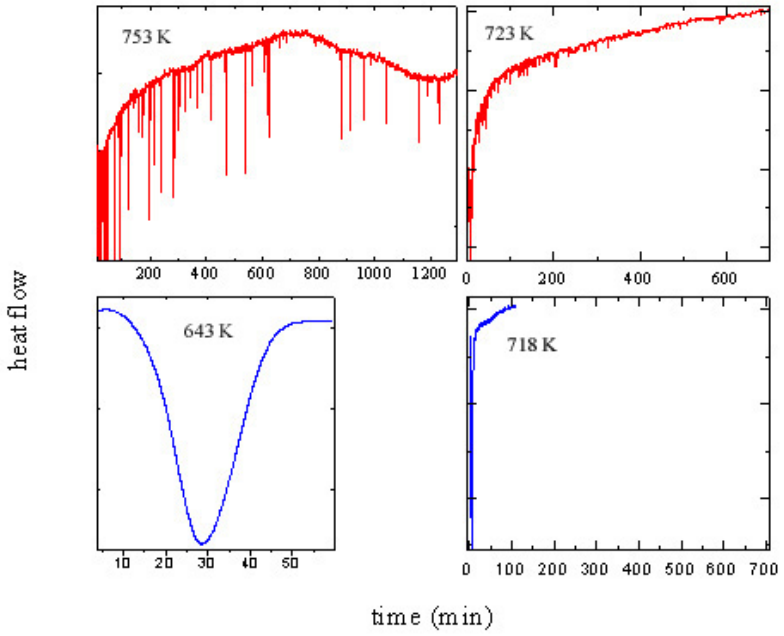

Figure 4

Theoretical analysis shows that it is not possible to describe the entire crystallization using one single steady state nucleation mechanism. Since the time scale to reach the onset of crystallization (~$t_{1\%}$) is up to three orders of magnitude larger than the time scale for the completion of each crystallization event itself ($t_{90\%}$-$t_{1\%}$), the subsequent rapid crystallization requires a sudden dramatic increase in the nucleation rate. This can be explained qualitatively in the following way. The first nucleus forms according to a very low initial steady state nucleation

rate I_{SS}. This nucleus, then, triggers rapid nucleation by, for instance, changing the composition in its neighborhood causing a chain reaction-like process. We observed a dramatic change of the crystallization of an ensemble of particles from individual crystallization above 723 K to collective crystallization below 718 K (Fig. 4). Here, crystallization must be diffusion controlled such that every particle behaves the same way. This suggests that no considerable nucleation barrier for the formation of crystals exists below the transition range.

Crystallization in $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ Melts

In the past several years, a large number of experiments have been performed to study the effects of thermal treatments on BMG. In particular, the Vit1 has been investigated extensively. Upon annealing above 613 K which is near the DSC (differential scanning calorimetry) glass transition temperature T_g and below a critical temperature T_c of around 673 K, Vit1 has been found to decompose into two supercooled liquid phases as revealed by the appearance of an interference peak in SANS. Further annealing results in precipitation of crystalline phases. However, there are uncertainties regarding the nature of the precipitated nanocrystalline phases and it is difficult to determine quantitatively the volume fraction of nanocrystals in the amorphous matrix. Using ^{9}Be NMR, XRD, and SANS we found that the formation of a Be-containing icosahedral phase plays an important role in the devitrification process of Vit1 below T_c. Above T_c, Be_2Zr forms along with Zr_2Cu and other crystalline phases. XRD pattern hints at some possible structural link between the icosahedral phase in Vit1 and Be_2Zr and Zr_2Cu. Our NMR and XRD results demonstrate that Be participates in the formation of the icosahedral phase in Vit1 upon annealing below T_c. The formation of the icosahedral phase in Vit1, preceded by the decomposition of the supercooled liquid, is not polymorphic and probably occurs in a Ti-poor (Be-rich) region. The fine-grained structure produced by decomposition of the supercooled liquid in Vit1 limits the grain size of the icosahedral phase and leads to broad XRD diffraction peaks compared to that observed in Vit4. Above T_c, annealing produces Be_2Zr and Zr_2Cu, which might originate from the decomposition of the metastable icosahedral phase. The XRD data indicates that there is a structural relationship between the icosahedral phase formed in Vit1 upon annealing and the Be_2Zr and Zr_2Cu crystalline phases.

Papers published in peer-reviewed journals

1. Diffusion mechanisms in metallic supercooled liquids and glasses
   X.-P. Tang, Ulrich Geyer, Ralf Busch, William L. Johnson, and Yue Wu,
   Nature **402**, 160-162 (1999).

2. Transition from Nucleation Controlled to Growth Controlled Crystallization in $Pd_{43}Ni_{10}Cu_{27}P_{20}$ Melts
   J. Schroers, Y. Wu, R. Busch, and W. L. Johnson
   Acta Materialia **49** (14), 2773-2781 (2001).

3
   Jörg F. Löffler, X.-P. Tang, Yue Wu and William L. Johnson
   Materials Research Society Symposium Proceedings **644**, L1.9.1-L1.9.6 (2001).

4. Heterogeneous Influences on the Crystallization of $Pd_{43}Ni_{10}Cu_{27}P_{20}$
   J. Schroers, Y. Wu, and W. L. Johnson
   Philosophical Magazine A **82**, 1207-1217 (2002)

5. Quasicrystalline Compounds; Metallic Glasses
   X.-P. Tang and Yue Wu

Encyclopedia of Nuclear Magnetic Resonance Volume 9, Advances in NMR (eds. D. M. Grant and R. K. Harris, John Wiley&Sons, Chichester, 2002). ISBN: 0-471-49082-2. p729-736.

6. Devitrification of Bulk Metallic Glass $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ Studied by XRD, SANS, and NMR

   X.-P. Tang, J. F. Löffler, W. L. Johnson, and Y. Wu
   Journal of Non-Crystalline Solids **317**, 118-122 (2003).

.

Manuscripts submitted

1. Crossover of Microscopic Dynamics in Metallic Supercooled Liquid Observed by NMR
   Lilong Li, Jan Schroers, and Yue Wu

Participating scientific personnel

Yue Wu (PI), Xiaoping Tang (postdoctoral fellow), Lilong Li (graduate student)